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# **Evaluation of CO<sub>2</sub> and CO Dopants in Hydrogen to Reduce Hydrogen Permeation in the Stirling Engine Heater Head Tube Alloy CG-27**

John A. Misencik  
National Aeronautics and Space Administration  
Lewis Research Center

July 1983

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AUTH: A/MISENCIK, J. A.

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MAJS: /\*ADDITIVES/\*CARBON DIOXIDE/\*CARBON MONOXIDE/\*HEAT RESISTANT ALLOYS/\*  
HYDROGEN/\*PERMEATING/\*PIPES (TUBES)/\*STIRLING CYCLE

MINS: / CONCENTRATION (COMPOSITION)/ DIESEL FUELS/ EXPOSURE

PBA: Author

ABS: Tubes of CG-27 alloy, filled with hydrogen doped with various amounts of  
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ENTER:





**Evaluation of CO<sub>2</sub> and CO Dopants  
in Hydrogen to Reduce Hydrogen  
Permeation in the Stirling Engine  
Heater Head Tube Alloy CG-27**

John A. Misencik  
National Aeronautics and Space Administration  
Lewis Research Center  
Cleveland, Ohio 44135

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# EVALUATION OF CO<sub>2</sub> AND CO DOPANTS IN HYDROGEN TO REDUCE HYDROGEN PERMEATION IN THE STIRLING ENGINE HEATER HEAD TUBE ALLOY CG-27

John A. Misencik

National Aeronautics and Space Administration  
Lewis Research Center  
Cleveland, Ohio 44135

## SUMMARY

An experimental program was conducted to determine the effectiveness of low concentrations of carbon dioxide and carbon monoxide in reducing hydrogen permeation in a candidate Stirling engine heater head tube alloy. Tubes of CG-27 alloy were pressurized with hydrogen doped with various amounts of carbon dioxide or carbon monoxide. The tubes were heated in a diesel-fuel-fired Stirling engine materials simulator test rig for 100 hours at 820° C and 15 MPa pressure. The effectiveness of the low levels (0.05 to 1.0 volume percent) of dopants in reducing hydrogen permeation through the hot tube walls was measured from pressure decay-time curves. This was done for one series of tubes in the clean, as-heat treated condition. A second series of tubes that had previously been pre-oxidized by heating for 100 hours in hydrogen doped with 1.0 volume percent carbon dioxide were also tested to determine if lower levels of dopant could maintain the low hydrogen permeation achieved by doping with 1.0 volume percent CO<sub>2</sub>. Carbon dioxide was most effective in reducing hydrogen permeation in clean and in prior exposed tubes. After heating initially clean tubes for 100 hours at 820° C and 15 MPa pressure using 1.0, 0.1, and 0.05 volume percent CO<sub>2</sub>, hydrogen permeability coefficients of 0.5, 1.0, and  $1.8 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> resulted, respectively. For pre-oxidized tubes the 0.1 volume percent CO<sub>2</sub> maintained the value of  $0.5 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> while the value increased to  $0.7 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> for the 0.05 volume percent CO<sub>2</sub> level. Carbon monoxide as a dopant was less effective than carbon dioxide at a given dopant level. For example, the 0.05 volume percent CO dopant level resulted in a hydrogen permeability coefficient of  $2.5 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> for clean tubes and a value of  $1.0 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> for pre-oxidized tubes. These results are in agreement with the concept of the carbon dioxide and carbon monoxide dopants reacting with the tube alloy to form an oxide film on the internal tube wall which acts as a barrier to hydrogen permeation. Lower permeability rates achieved with carbon dioxide and with higher dopant levels can be attributed to a greater concentration of oxygen available for oxide film formation as compared to carbon monoxide as the dopant.

## INTRODUCTION

The work described in this report was conducted as part of the continuing supporting research and technology activities under the DOE-NASA Stirling Engine Highway Vehicle Systems Program (ref. 1). The Stirling engine, utilizing hydrogen as the work fluid, is currently designed to operate at high pressures (to 21 MPa) and at a high operating temperature of 820° C to achieve maximum engine efficiency required for commercial highway vehicles.

Retention of hydrogen in the hot heater head tubes is a problem, as the hydrogen readily permeates the hot tube walls. Prior work (refs. 2 and 3) has shown that oxygen contents as low as 350 parts per million in the hydrogen can substantially reduce hydrogen permeation through the tube walls while at the 760° to 820° C temperature level. Reduction in hydrogen permeation of an order of magnitude has been achieved in some alloys. It has been postulated that this reduction in hydrogen permeation is the result of a thin oxide layer formed on the inner surface of the tube, coupled with the formation of a thick adherent oxide layer on the fire-side of the tubes (refs. 2, 4, and 5). A further study (ref. 6) has shown that carbon monoxide and carbon dioxide, in the levels of 0.2 to 5.0 volume percent in hydrogen are both effective in reducing the hydrogen permeation at 760° and 820° C in all the candidate heater tube alloys studied. Carbon dioxide was effective at levels as low as 0.2 percent and carbon monoxide was only slightly less effective at the levels below 2.0 percent. Based on the results of this work (ref. 6), a conservative 1.0 percent carbon dioxide level was selected for use in a 3500-hour endurance run. The results for the 3500-hour endurance run will be reported in a separate report.

The purpose of the work described in this report was two-fold. First, the work sought to determine if reduced dopant levels of CO<sub>2</sub> and CO in hydrogen can be effective in reducing hydrogen permeation at 820° C in clean tubes of CG-27 since some performance penalty results upon doping the hydrogen working fluid with 1 volume percent CO<sub>2</sub>. Secondly, the work sought to determine if reduced dopant levels can be effective in maintaining low level of hydrogen permeation in tubes that have previously been subjected to pre-oxidation by heating in hydrogen doped with higher (1.0 percent CO<sub>2</sub>) levels of dopant. The selection of the CG-27 alloy for this work was based on the results of previously completed 3500-hour endurance runs which identified this alloy as having the potential of meeting the requirements currently envisioned for the automotive Stirling engine.

## EXPERIMENTAL PROCEDURES

### Materials

The CG-27 alloy used in this study was obtained commercially in the form of tubing with an outside diameter of 4.5 mm, and a wall thickness of 0.8 mm. The tubing was fabricated by seamless drawing. Prior to use in the dopant runs the CG-27 tubing was heat treated to the following schedule:

1149° C (2100° F) - Vac/10 min./furnace cool  
788° C (1450° F) - Vac/16 hr/cool to 1200° F  
649° C (1200° F) - Vac/24 hr/furnace cool

Chemical analysis of the drawn tubing is shown in table I. The analysis was made at Lewis Research Center and is given in weight percent. The alloy contains 36 percent nickel, 13 percent chromium, 5.5 percent molybdenum, 2.6 percent titanium, 1.7 percent aluminum and 0.9 percent columbium, and the balance iron.

Chemical analyses of the hydrogen doped with the various gases are shown in table II. These include hydrogen doped with 1.0, 0.1, and 0.05 volume per-

cent carbon dioxide; and hydrogen doped with 1.0, 0.5, 0.2, and 0.05 volume percent carbon monoxide. All gas mixtures were made using propellant hydrogen as the base.

### Stirling Engine Simulator Rig

The Stirling engine simulator rig used in this study was the same as that used previously in the endurance runs and dopant study described in references 2, 3, and 6. The rig consists primarily of a combustion gas heating chamber with auxiliary heating control and gas management systems. A schematic drawing of the heating chamber is shown in figure 1. A detailed description of the rig and its operation is given in reference 2. The rig has 12 test modules located at the top of the heating chamber. These modules are installed by insertion into holes spaced around the top of the heating chamber and bolting each in place. Each module equipped with a pressure transducer with a range from 0 to 34 MPa. These transducers are strain gage devices made of 304 stainless steel and are sealed to the module with an elastometric "O" ring. Cooling of the modules near the transducer is achieved by situating the modules on water-cooled copper plates. This can be seen in figure 1. The tubing alloys were attached to the module by gas-tight mechanical fasteners and were in the form of "hairpins" as shown in figure 2. Each leg of the "hairpin" was 30.5 cm long with 2.5 cm between legs. Four of these "hairpin" tubes were attached to a copper module with internal passages and external tubes and valves for filling each module with the proper gas. The "hairpin" tubes were connected in series and were filled through the tubing and valves located on top of each module. A module with "hairpin" tubes attached is shown in figure 3. Also shown in figure 3 is the thermocouple that was attached at the bottom of the "hairpin" tube and the lead to the pressure transducer that was located adjacent to the thermocouple plug at the top of the module.

A dopant run consisted of a series of 5-hour cycles to obtain a total time of 100 hours. All dopant runs in this report were conducted at 820° C. A typical heating cycle consisted of a 6 to 10 minute preheat to operating temperature (820° C), a 5-hour hold at temperature, and a cooldown to near room temperature. The cooldown time between cycles as 1 hour or longer. After cooldown to about 25° C, the tubes were vented, the pressure transducer was rezeroed, and the tubes refilled. The pressure reading used for permeation calculations were made at the start of each 5-hour cycle (approx. 6 to 10 minutes into the cycle) and at the end of 5 hours at temperature, just prior to cooldown.

### Metallography

Metallographic specimens were sectioned from one "hairpin" of each module after exposure. The specimens were sectioned from the hottest zone of the tube, (approx. 17 cm from the bend), polished and etched using an etchant of 33 percent nitric acid, 33 percent acetic acid, 33 percent H<sub>2</sub>O and 1 percent HF, and examined at magnifications of 100x and 500x.

## RESULTS AND DISCUSSION

### Pressure-Time Relationships

Hydrogen pressure-time data for the CG-27 alloy during five selected cycles of the 100-hour runs with all the dopants used are shown in table III A, B, C. The 5-hour cycles selected were for 0-5, 20-25, 45-50, 70-75, and 95-100 hours.

The maximum pressure at the start of the 5-hour cycle and the pressure at the end of the 5-hour cycle are given for the five selected cycles. Table II A gives the data for dopant runs conducted with 1.0, 0.1, and 0.05 volume percent carbon dioxide in hydrogen. The dopant runs were conducted on clean CG-27 tubes. Table II B gives the data for the dopant runs conducted with 1.0, 0.5, 0.2, and 0.05 volume percent carbon monoxide in hydrogen. These dopant runs were also conducted on clean CG-27 tubes. Table III C gives the data for the dopant runs that were conducted on tubes that had previously been exposed for 100 hours at 820° C to hydrogen doped with 1.0 volume percent carbon dioxide. The dopant runs were conducted with 0.1 and 0.05 volume percent carbon dioxide and 1.0, 0.5, 0.2, and 0.05 volume percent carbon monoxide.

The pressure decay data for the dopant run conducted with 1.0 volume percent carbon dioxide are plotted in figure 4. This figure shows a rapid rise in pressure, to approximately 15 MPa usually within 10 minutes, and then a decay in pressure during the remainder for the 5-hour cycle. This pressure decay with time at temperature results from hydrogen permeating through the hot tube walls. The rate of pressure decay has been shown to vary with alloy, dopant species, species concentration and time during the exposure run. For comparative purposes data from reference 6 for the N155 alloy, currently used in the Stirling engine are shown in figure 5(a). With UHP hydrogen, the pressure was substantially below 1.0 MPa after 4 hours and nearly zero after 5 hours for each of the cycles shown, and indication of rapid hydrogen loss through the hot tube wall. Figure 5(b), also for N155 (ref. 6) but with hydrogen doped with 1 volume percent carbon dioxide, shows that there pressure decay for the first 5-hour cycle (0-5) was similar to that with UHP hydrogen. However, the pressure decays for the subsequent cycles were greatly reduced using the hydrogen doped with 1 percent carbon dioxide. In comparing figure 4 with figure 5(b), note that the starting pressure was approximately 21 MPa in figure 5(b) whereas the starting pressure in figure 4 was approximately 15 MPa. Comparison of permeability coefficients shown that the 1.0 volume percent carbon dioxide dopant in hydrogen was more effective in the CG-27,  $0.5 \times 10^{-6} \text{ cm}^2/\text{sec MPa}^{1/2}$  compared with  $1.0 \times 10^{-6} \text{ cm}^2/\text{sec MPa}^{1/2}$  for the N155 alloy.

### Hydrogen Permeation

Permeability coefficients,  $\phi$ , were calculated for each 5-hour cycle throughout the 100-hour dopant runs by using the data from the pressure drop curves and the equation from reference 2.

$$P = P_0^{1/2} - \phi \frac{A P T t}{2 \lambda V T_s}$$

where

P	pressure in closed system, MPa
P <sub>0</sub>	original pressure, MPa
A	permeated area, cm <sup>3</sup>
P	standard pressure, MPa
T <sub>s</sub>	temperature of system, K
t	time, sec
l	membrane thickness, cm
V	volume of system, cm <sup>3</sup>
T <sub>s</sub>	standard temperature, K

It should be noted that the Stirling materials simulator test rig, modules and tubes were not expressly designed for the measurement of permeation, but rather were designed for environmental endurance testing to determine the effects of burner and hydrogen environments on the life of tubes under pressure. Thus the permeation numbers should be considered as "apparent" permeation coefficients. However, they are valuable in rating of dopants in hydrogen.

The calculated permeation coefficients for the CG-27 alloy pressurized with hydrogen doped with the various dopants and tested at 820° C are shown in Table IV, data for the selected cycles during the 100-hour run, 5, 10, 15, 20, 25, 50, 75, and 100 hours are given. The data are for results obtained on clean tubes and on tubes that had previously been run for 100 hours with 1.0 volume percent carbon dioxide. The 1.0 percent carbon dioxide dopant level was run on 6 modules with 4 clean tubes in each module. The data represent an average for the 6 modules. The remaining dopants were run on individual modules. The data are shown plotted in figures 6 to 9 and are summarized in figures 10 and 11.

#### Clean Tubes - Carbon Dioxide Dopant

The calculated permeability coefficients for clean CG-27 tubing using hydrogen doped with 1.0, 0.1, and 0.05 volume percent carbon dioxide from table IV are plotted in figure 6. It is clearly shown in figure 6 that the larger the amount of carbon dioxide dopant the greater, the reduction in hydrogen permeability coefficient after 100 hours of testing. The 1.0 volume percent carbon dioxide was the most effective and 0.05 volume percent carbon dioxide was the least effective. The permeability coefficient at the end of the 100-hour test were 0.49, 1.06, and  $1.79 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> for CO<sub>2</sub> levels of 1.0, 0.1, and 0.05 volume percent respectively.

#### Clean Tubes - Carbon Monoxide Dopant

The calculated permeability coefficients for initially clean CG-27 tubing using hydrogen doped with 1.0, 0.5, 0.2, and 0.05 volume percent carbon monoxide from table IV are plotted in figure 7. This also clearly shows that the larger the amount of carbon monoxide dopant, the greater the reduction in hydrogen permeability coefficient,  $\phi$ . Both the 1.0 and 0.5 volume percent carbon monoxide levels were very effective - reducing  $\phi$  to  $0.58 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> and  $0.66 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup>, respectively. The 0.2 volume percent reduced the hydrogen permeability coefficient to  $1.57 \times 10^{-6}$  while the 0.05 volume percent carbon monoxide level resulted in a  $\phi$  of  $2.26 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup>.

A comparison of the hydrogen permeability coefficient after testing for 100 hours with various CO<sub>2</sub> and CO dopant levels is shown in figure 8. It can be seen in figure 8 that the carbon dioxide dopant was more effective at any given dopant level tested, however, at the 1.0 volume percent level the hydrogen permeability coefficient,  $\phi$ , was not greatly different,  $\phi = 0.49 \times 10^{-6}$  for 1.0 volume percent CO<sub>2</sub> and  $\phi = 0.58 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> for 1.0 volume percent CO.

#### Prior Exposed Tubes - Carbon Dioxide Dopant

Tubes of CG-27 alloy were exposed for 100 hours in 1.0 volume percent CO<sub>2</sub> at 820° C and 15 MPa pressure to pre-oxidize the internal tube wall. Subsequent to this treatment the tubes were tested for a second 100 hours using lower dopant levels.

The pre-oxidization treatment resulted in an average permeability coefficient of  $0.49 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> (table IV) after 100 hour exposure. Subsequent exposure for an additional 100 hours resulted in permeability coefficients,  $\phi$ , of  $0.43 \times 10^{-6}$  and  $0.65 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> for the 0.1 and 0.05 volume percent carbon dioxide levels, respectively. These data plotted in figure 9 show that the 0.1 volume percent carbon dioxide was effective in maintaining the low hydrogen permeability coefficient during the 100-hour run. The 0.05 volume percent carbon dioxide dopant did not maintain the low level ( $0.49 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup>) obtained with the 1.0 volume percent carbon dioxide, however, the hydrogen permeability coefficient did stabilize after 50 hours at a  $\phi$  of  $0.65 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup>. The sharp rise in the curve for 0.05 volume percent carbon dioxide, plotted as a dotted line in figure 9 is not real but is the result of a temperature control problem during this time period.

#### Prior Exposed Tubes - Carbon Monoxide Dopant

The average permeability coefficient after the 100-hour pre-oxidization treatment with 1.0 volume percent carbon dioxide was  $0.49 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup>. Subsequent exposure for an additional 100 hours to hydrogen doped with 1.0, 0.5, 0.2, and 0.05 volume percent carbon monoxide resulted in hydrogen permeability coefficients,  $\phi$ , of 0.58, 0.40, 0.66, and  $0.99 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup>, respectively. These data plotted in figure 10, show that the 0.5 volume percent CO was the most effective dopant level in those tubes that had received the pre-oxidization treatment having  $\phi = 0.40 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> compared to a  $0.58 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup> for 1.0 volume percent CO. It appears the the 0.05 volume percent CO is not as effective in maintaining the low level of hydrogen permeability achieved with 1.0 volume percent CO<sub>2</sub>.

The effect of the two dopant gases (CO<sub>2</sub> and CO) on the hydrogen permeability coefficient,  $\phi$ , are compared in figure 11 which shows the hydrogen permeability coefficient,  $\phi$ , plotted as a function of dopant level in the hydrogen. The average  $\phi$ , obtained after the pre-oxidization treatment is shown at a value of  $\phi = 0.49 \times 10^{-6}$  cm<sup>2</sup>/sec MPa<sup>1/2</sup>. Both the 0.1 volume percent CO<sub>2</sub> and 0.5 volume percent CO dopants further lowered the hydrogen permeability coefficient from the obtained from the pre-oxidization treatment. The remaining dopant levels experienced an increase in permeability after the additional 100 hours of exposure. The 1.0 volume percent CO having a higher



permeability coefficient than the 0.5 volume percent CO content was surprising as one would expect the 1.0 volume percent CO level to be more effective than the 0.5 volume percent level. A similar behavior was found in the original dopant studies (ref. 6) where the higher dopant level, 5 volume percent (CO<sub>2</sub> or CO) was less effective than the lower 0.5 and 1.0 volume percent levels. One possible explanation for this behavior is that the larger amounts of dopant result in thicker oxide layers that can crack and thus cause hydrogen permeation, (ref. 7).

### Microstructure

The microstructure of the as-heat treated CG-27 tubes prior to exposure to CO<sub>2</sub>/CO hydrogen doped gases are shown in figure 12. The microstructure shows a mixed grain size, with an average grain size of 38  $\mu$ m. Precipitates, primarily within the grain matrix are also evident in figures 12(a) and (b).

Metallographic specimens are sectioned from a "hairpin" from each module after exposure. The specimens, sectioned from the hottest zone of the tube, (approx. 17 cm from bend), were polished, etched and examined at magnifications of 100 and 500x.

Cross-sections of a tube from each of the dopant runs are shown in figures 13(a) to (f) and 14(a) to (f) at a magnification of 100x. Figures 13(a) to (f) show the tube cross-section of those tubes that were exposed for 100 hours to hydrogen doped with 1.0, 0.5, 0.2, and 0.05 volume percent CO and 0.1 and 0.05 volume percent CO<sub>2</sub>, respectively. Figures 14(a) to (f) show the tube cross-sections of those tubes that were pre-exposed for 100 hours to hydrogen doped with 1.0 volume percent CO<sub>2</sub> followed by an additional 100 hours exposure to hydrogen doped with 1.0, 0.5, 0.2, and 0.05 volume percent and 0.1 and 0.05 volume percent CO<sub>2</sub>, respectively. Examination of the photomicrographs shown in figures 13(a) to (f) show little or no reaction or oxide on the inner or outer edges of the tubes. This can be seen more clearly at a magnification of 500x in figure 15 which shows the inner and outer edges of the tube cross-sections shown in the figure 13(a).

Examination of the photomicrographs shown in figures 14(a) to (f), which show the tube cross-sections of tubes that had been pre-exposed for 100 hours to hydrogen doped with 1.0 volume percent CO<sub>2</sub> prior to exposure with hydrogen containing reduced dopants, shows a surface reaction has taken place at the inner and outer edges of the tubes. Also there is some evidence of a slight oxide layer present on the inner and outer edges of the tubes. This can be seen more clearly in figures 16 and 17 which show the inner and outer edges of the tubes, at 500x, previously shown in figures 14(c) and (d), respectively, at 100x. The lack of any appreciable oxide on the outside edges of the tubes, even those exposed for 200 hours, indicates that the CG-27 alloy is not adversely affected by the fireside environment of burning diesel fuel at 820° C.

### SUMMARY OF RESULTS

The experimental investigation to determine: if reduced dopant levels in hydrogen can be effective in reducing hydrogen permeation through initially clean CG-27 at 820° C and 15 MPa pressure; and if reduced dopant levels in

hydrogen can maintain the low levels of hydrogen permeation resulting from prior exposure to hydrogen doped with 1.0 volume percent carbon dioxide, had the following results:

#### Clean Tubes

- (1) The 1.0 volume percent CO<sub>2</sub> and 1.0 volume percent CO levels in hydrogen were effective in reducing hydrogen permeation clean tubes of CG-27 at 820° C and 15 MPa pressure.
- (2) The 0.1 volume percent CO<sub>2</sub> and 0.5 and 0.2 volume percent CO levels in hydrogen reduced the apparent permeability coefficient to one-half that obtained after the initial 5 hours in clean tubes of CG-27.
- (3) The low levels of CO<sub>2</sub> and CO in hydrogen (0.05 volume percent) were not as effective as dopants for use on clean CG-27 tubing at 820° C and 15 MPa pressure.

#### Prior Exposed Tubes

- (4) The 0.1 volume percent CO<sub>2</sub> and 0.5 volume percent CO dopant levels were effective in further reducing the low level of hydrogen permeation obtained on tubes that had prior exposure for 100 hours with 1.0 volume percent CO<sub>2</sub>.
- (5) The lowest levels of CO<sub>2</sub> and CO (0.05 volume percent) in hydrogen were not effective in maintaining the low level of hydrogen permeation obtained by exposure for 100 hours at 820° C in 1.0 volume percent CO<sub>2</sub>. However, all hydrogen permeability coefficients,  $\phi$ , obtained were below  $1.0 \times 10^{-6} \text{ cm}^2/\text{sec MPa}^{1/2}$ .

#### CONCLUDING REMARKS

The results of this investigation show that the hydrogen permeation through hot tube walls as reflected by the hydrogen permeability coefficient,  $\phi$ , can be substantially reduced using 1.0 volume percent CO<sub>2</sub> as a dopant in the hydrogen. Also it has been shown that the reduced hydrogen permeability obtained using hydrogen doped with 1.0 volume percent CO<sub>2</sub> for a limited time (100 hr) can be maintained by using hydrogen with reduced CO-CO<sub>2</sub> dopant levels. It has been postulated (ref. 3) that the oxygen in the hydrogen forms a thin adherent oxide on the inside surface of the tube, which greatly reduces the hydrogen permeation though the tube was at elevated temperatures. It was found (ref. 3) that the amount of oxygen required to reduce hydrogen permeation in the hydrogen was in the order of 350 parts per million (ppm). Assuming that all the oxygen contained in the CO-CO<sub>2</sub> doped hydrogen is available to form the oxide film, the 350 ppm oxygen level translates to 0.046 volume percent CO<sub>2</sub> or 0.06 volume percent CO. A 500 ppm oxygen level, which is not uncommon in commercial grade hydrogen, translates to 0.07 volume percent CO<sub>2</sub> or 0.087 volume percent CO. The 0.1 volume percent CO<sub>2</sub> was very effective in maintaining a low level of hydrogen permeation in tubes that had previously been exposed for 100 hours to hydrogen doped with 1.0 volume percent CO<sub>2</sub>. Thus it appears feasible that the low levels of hydrogen permeation obtained with limited exposure to hydrogen doped with 1.0 volume percent CO<sub>2</sub> can be

maintained using commercial hydrogen which may contain 350-500 ppm of oxygen. In order to verify this, it is recommended that limited further studies be conducted.

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TABLE I. - COMPOSITION OF  
CG-27 SEAMLESS TUBING  
WEIGHT PERCENT  
(Except where noted)

Element	Heat B 980052
Cr	13.31
Ni	36.16
Mn	<.10
Mo	5.52
Ti	2.58
Cb	.94
Si	.12
Al	1.68
C	.056
B	.006
P	.022
S	.002
N	<sup>a</sup> 62
O	<sup>a</sup> 20
H	<sup>a</sup> .0014
Bal Fe	

<sup>a</sup>Parts per million.

TABLE II. - COMPSITION OF CO AND CO<sub>2</sub> DOPED HYDROGEN

Dopant level nominal	Analysis					
	CO	CO <sub>2</sub>	O <sub>2</sub>	Ar	N <sub>2</sub>	CH <sub>4</sub>
	Volume percent	Volume percent	Volume percent	Volume percent	Volume percent	Volume percent
1.0 CO	1.1029	0.0000	0.0000	0.0000	0.000	0.0156
0.5 CO	.49	-----	-----	-----	-----	-----
0.2 CO	.22	-----	-----	-----	-----	-----
0.05 CO	.051	-----	-----	-----	-----	-----
1.0 CO <sub>2</sub>	-----	.988	.0000	.0000	.0000	.0171
0.1 CO <sub>2</sub>	-----	.107	-----	-----	-----	-----
0.05 CO <sub>2</sub>	-----	.055	-----	-----	-----	-----

TABLE III. - SELECTED PRESSURE DECAY DATA DURING 100 HOUR TEST RUNS

(a) Clean tubes, Dopant - Carbon Dioxide, CO<sub>2</sub>.

Time during 100 hour run, hr	1.0 percent CO <sub>2</sub>		0.1 percent CO <sub>2</sub>		0.05 percent CO <sub>2</sub>	
	Average pressure (6 tubes)		Pressure		Pressure	
	Start	End	Start	End	Start	End
	MPa	MPa	MPa	MPa	MPa	MPa
0-5	15.56	4.81	14.82	3.52	15.72	4.48
5-10	14.38	7.62	14.89	5.72	15.44	6.90
10-15	15.65	9.51	15.03	7.10	16.00	4.96
15-20	15.11	9.66	15.72	8.41	15.51	6.76
20-25	15.58	10.57	15.38	8.41	15.72	4.91
45-50	14.88	11.29	16.06	9.86	16.00	5.31
70-75	15.59	11.87	16.06	10.55	15.31	5.65
95-100	14.84	12.05	16.06	10.44	15.31	6.21

(b) Clean tubes, Dopant - Carbon Dioxide, CO.

Time during 100 hour run, hr	1 percent CO		0.5 percent CO		0.2 percent CO		0.05 percent CO	
	Pressure		Pressure		Pressure		Pressure	
	Start	End	Start	End	Start	End	Start	End
	MPa	MPa	MPa	MPa	MPa	MPa	MPa	MPa
0-5	15.10	2.82	16.07	3.31	15.37	2.07	15.30	1.38
5-10	14.13	6.69	13.93	3.10	14.48	2.96	14.69	2.55
10-15	15.17	8.27	14.82	7.79	14.69	3.31	15.10	2.96
15-20	15.10	8.83	15.17	7.31	15.38	3.65	15.79	3.31
20-25	15.24	9.72	14.75	8.62	14.34	3.85	15.31	3.58
45-50	15.03	11.23	14.48	9.45	15.44	6.90	15.86	3.45
70-75	15.51	12.07	15.51	11.23	14.67	7.44	14.69	4.00
95-100	15.58	12.87	15.58	11.72	14.68	6.90	16.00	4.86

TABLE III. - CONCLUDED

(c) Tubes with 100 hours with H<sub>2</sub> + 1.0 volume percent CO<sub>2</sub> plus 100 hours with reduced dopant levels.

Time during 100 hour run, hr	1 percent CO <sub>2</sub> + 1 percent CO		1 percent CO <sub>2</sub> + 0.5 percent CO		1 percent CO <sub>2</sub> + 0.2 percent CO		1 percent CO <sub>2</sub> + 0.05 percent CO		1 percent CO <sub>2</sub> + 0.1 percent CO <sub>2</sub>		1 percent CO <sub>2</sub> + 0.05 percent CO <sub>2</sub>	
	Pressure		Pressure		Pressure		Pressure		Pressure		Pressure	
	Start	End	Start	End	Start	End	Start	End	Start	End	Start	End
	MPa	MPa	MPa	MPa	MPa	MPa	MPa	MPa	MPa	MPa	MPa	MPa
0-5	16.62	11.23	17.51	14.06	17.10	12.96	15.03	10.00	17.17	14.62	16.34	15.10
5-10	15.72	11.10	15.51	12.22	16.27	12.20	15.03	8.48	16.20	13.93	16.06	14.82
10-15	16.34	11.38	16.34	13.38	16.00	11.72	15.23	8.76	16.41	14.00	17.03	13.24
15-20	16.06	11.58	16.34	13.31	16.69	12.00	16.06	9.30	17.38	14.62	16.34	13.10
20-25	16.06	11.58	15.81	13.30	15.65	11.38	15.17	9.10	16.41	14.07	16.68	10.89
45-50	15.03	11.23	15.38	12.75	16.05	12.20	16.20	9.17	17.24	14.69	16.68	12.27
70-75	15.51	12.06	16.68	14.00	15.72	11.93	14.55	9.31	16.68	13.79	15.93	11.58
95-100	15.58	12.89	16.55	14.06	15.86	11.93	16.20	10.55	17.03	14.34	15.72	11.86

TABLE IV. - HYDROGEN PERMEABILITY COEFFICIENT DURING TEST RUNS WITH  
HYDROGEN DOPED WITH CO AND CO<sub>2</sub>

Time during 100 hour run, hr	Hydrogen permeability coefficient $\phi$ , cm <sup>2</sup> /sec MPa <sup>1/2</sup>												
	Temperature 820° C												
	Clean tubes							Tubes with 100 hr, Hz + 1 percent carbon dioxide					
	Dopant												
	Carbon dioxide, volume percent			Carbon monoxide, volume percent				Carbon dioxide, volume percent		Carbon monoxide, volume percent			
	a1.0	0.1	0.05	1.0	0.5	0.2	0.05	0.1	0.05	1.0	0.05	0.2	0.05
5	2.18	2.65	2.32	2.73	3.38	3.24	2.18	0.42	0.19	0.90	0.69	0.68	0.91
10	1.30	1.97	2.14	1.49	2.44	2.72	2.80	.38	.20	.80	.68	.69	1.23
15	1.11	1.62	2.33	1.28	1.31	2.63	2.65	.40	.58	.84	.49	.73	1.20
20	1.01	1.43	1.68	1.15	1.47	2.62	2.70	.44	.53	.76	.50	.79	1.22
25	.88	1.38	2.18	.99	1.01	2.38	2.63	.38	1.01	.76	.43	.73	1.11
50	.63	1.17	2.05	.67	.91	1.70	2.66	.41	.73	.67	.44	.58	1.26
75	.64	1.03	1.93	.59	.74	1.44	2.30	.46	.73	.64	.43	.64	.97
100	.49	1.06	1.79	.58	.66	1.57	2.26	.43	.65	.58	.40	.66	.99

<sup>a</sup>Average of 6 tests.





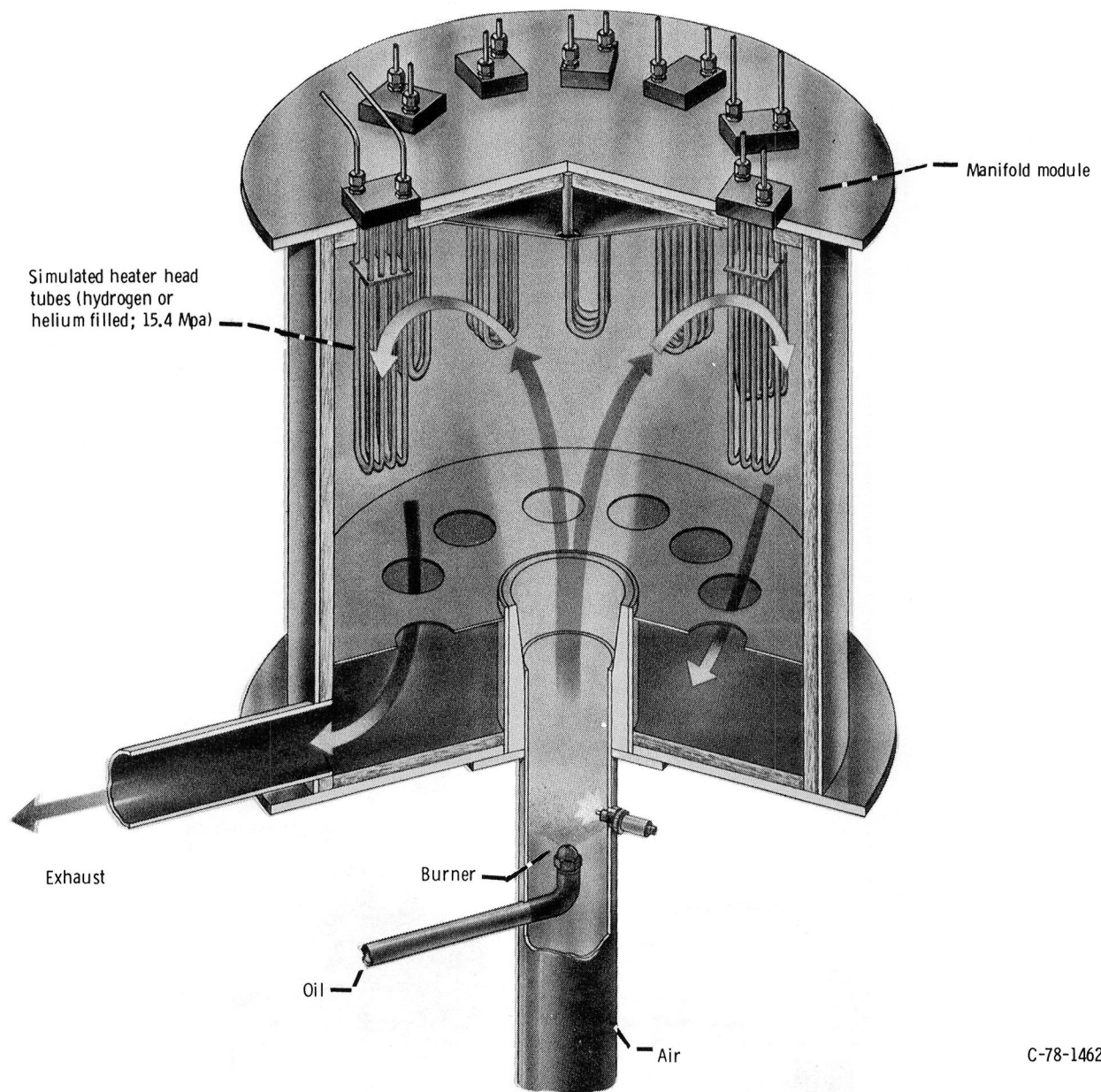


Figure 1. - Schematic representation of Stirling engine simulator materials test rig.

C-78-1462

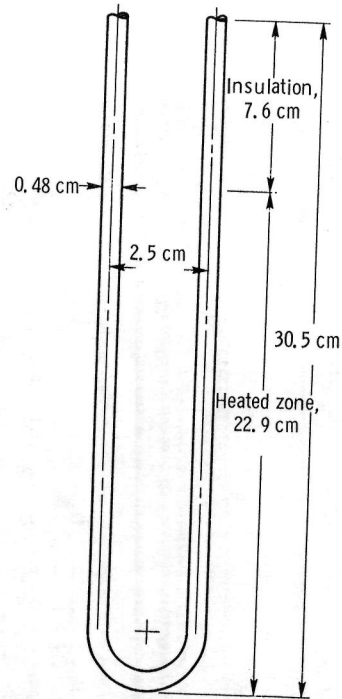
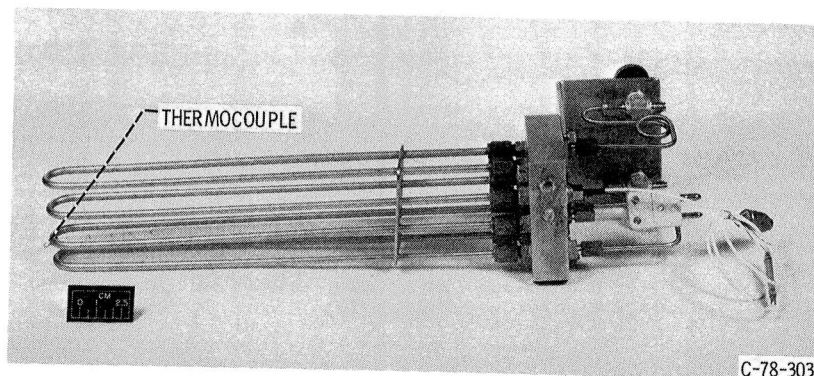


Figure 2. - Hairpin test specimen (not to scale).



C-78-303

Figure 3. - Test module for Stirling engine simulator materials test rig.

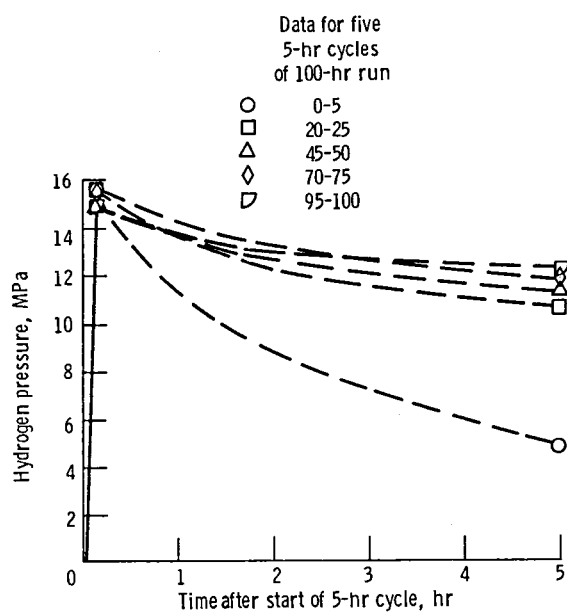


Figure 4 - Pressure decay curves for CG27 at 820° C.  
Hydrogen doped with 1% CO<sub>2</sub>.

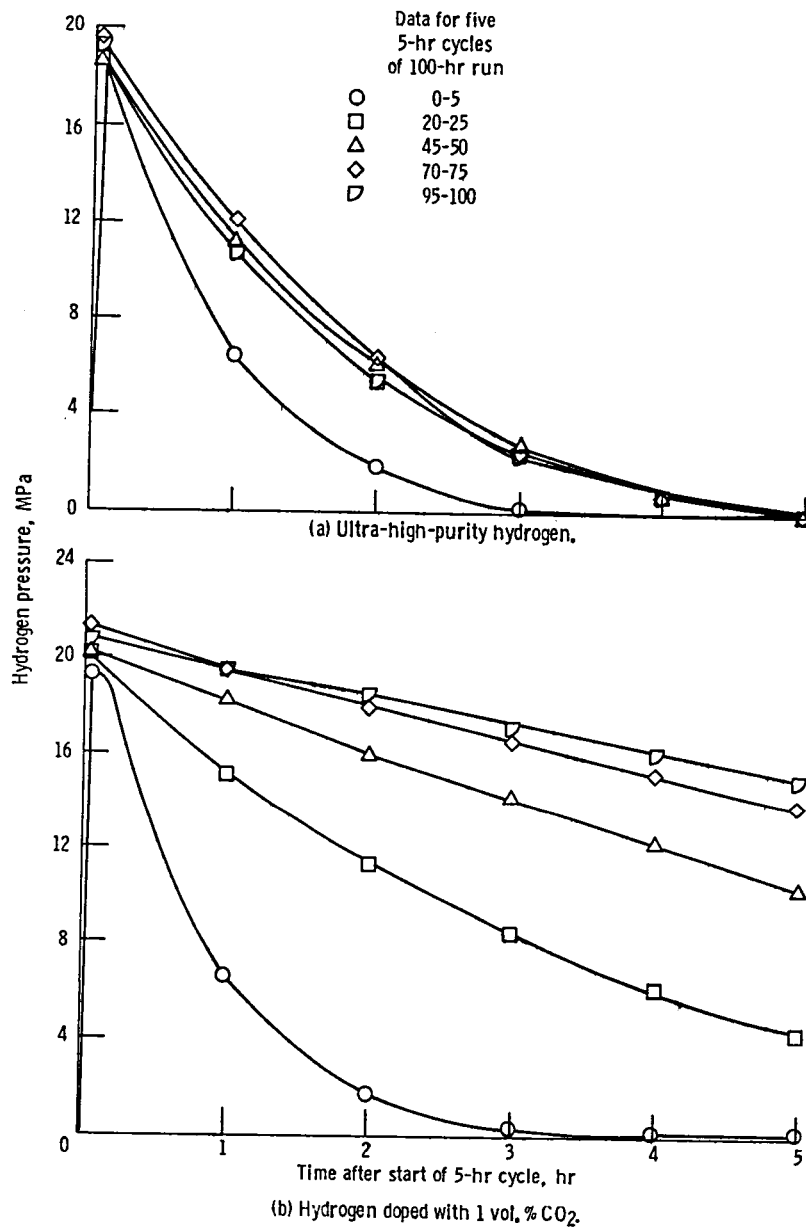


Figure 5. - Pressure decay curves for N-155 at 820°C.

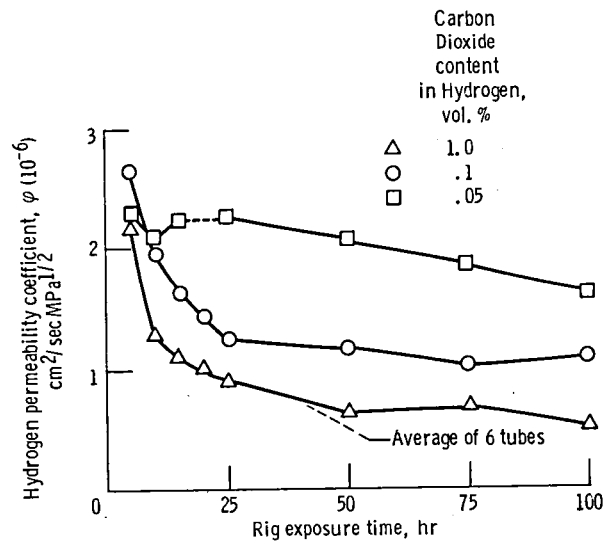


Figure 6. - Permeability coefficient as a function of elapsed time hydrogen doped with 1.0, 0.1 and 0.05% Carbon Dioxide in clean tubes of CG27.

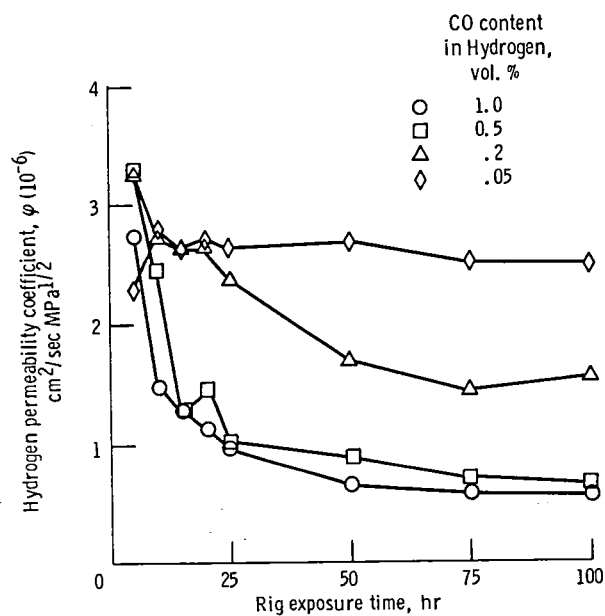


Figure 7. - Permeability coefficient as a function of elapsed time. Hydrogen doped with 1.0, 0.5, 0.2, 0.05% Carbon Monoxide in clean CG27 tubes.

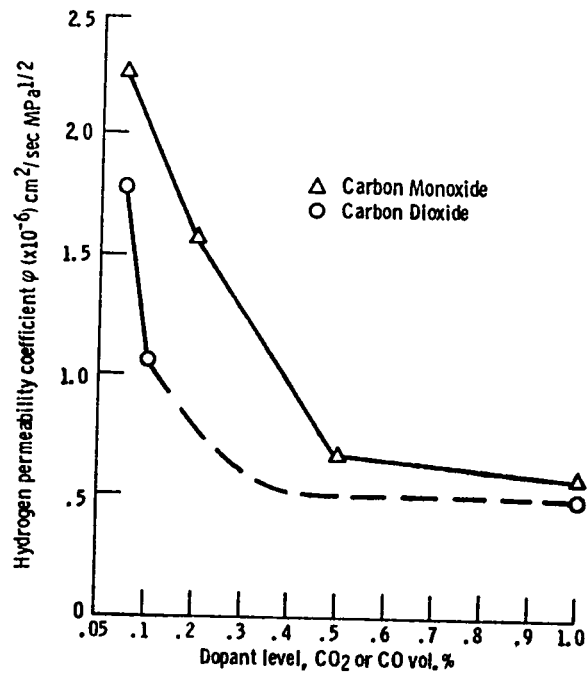


Figure 8. - Hydrogen permeability coefficient as a function of dopant level for clean tubes (after 100 hr at 820° C.

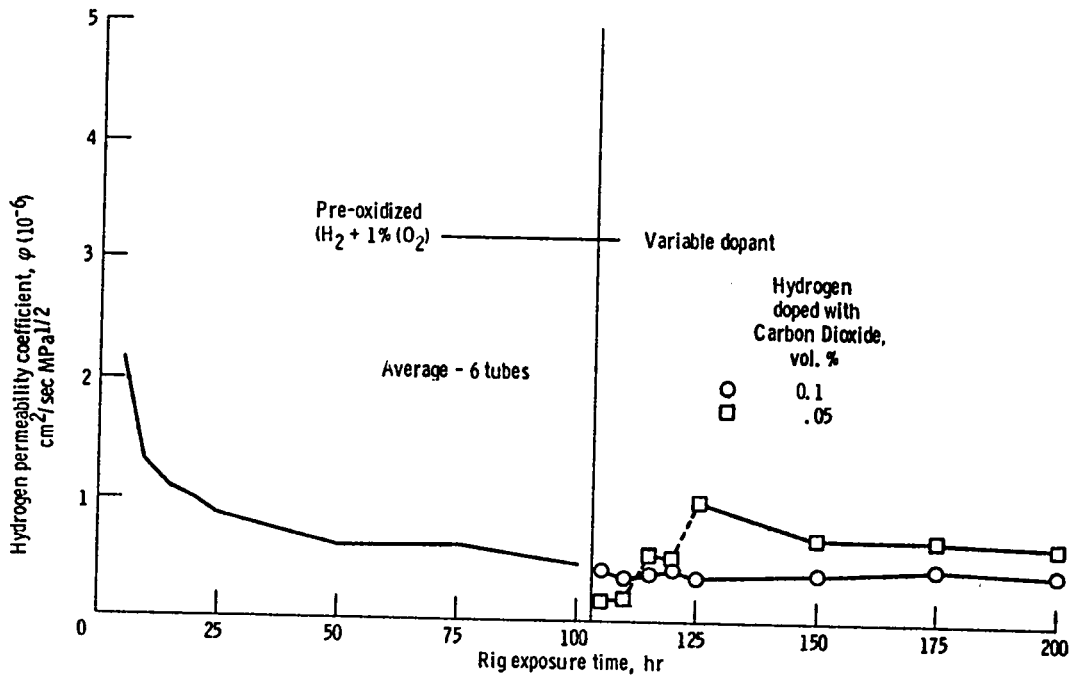


Figure 9. - Hydrogen permeability coefficient for CO<sub>2</sub> doped hydrogen as a function of elapsed time in pre-oxidized tubes.

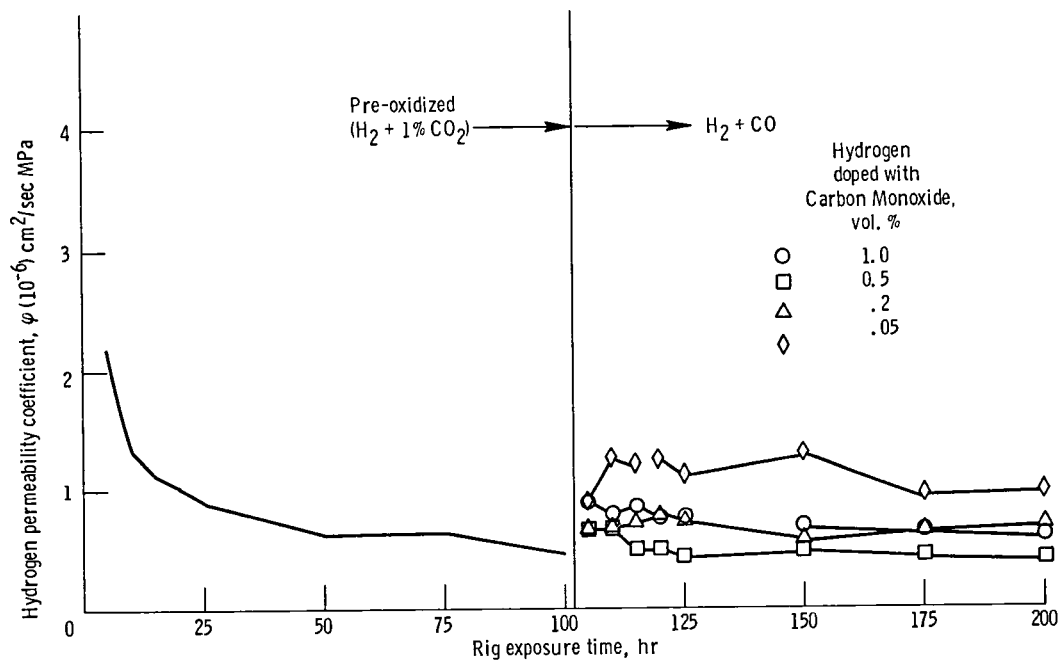


Figure 10. - Hydrogen permeability coefficient for CO doped hydrogen as a function of elapsed time in pre-oxidized tubes.

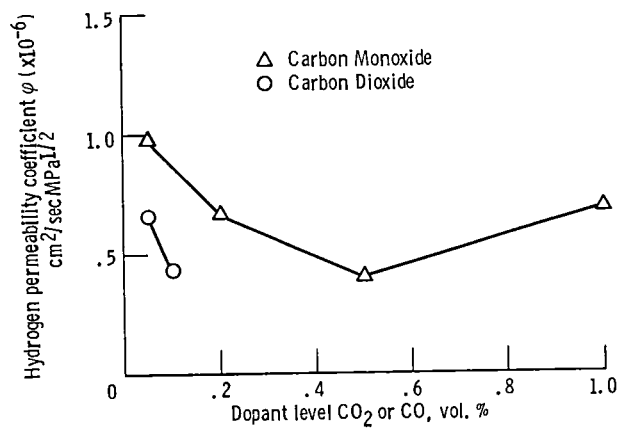
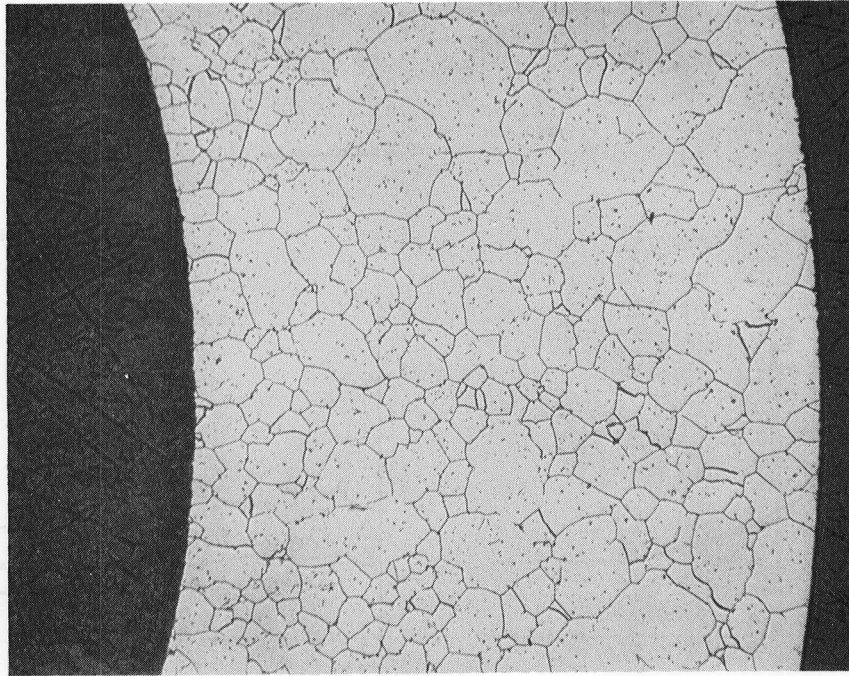
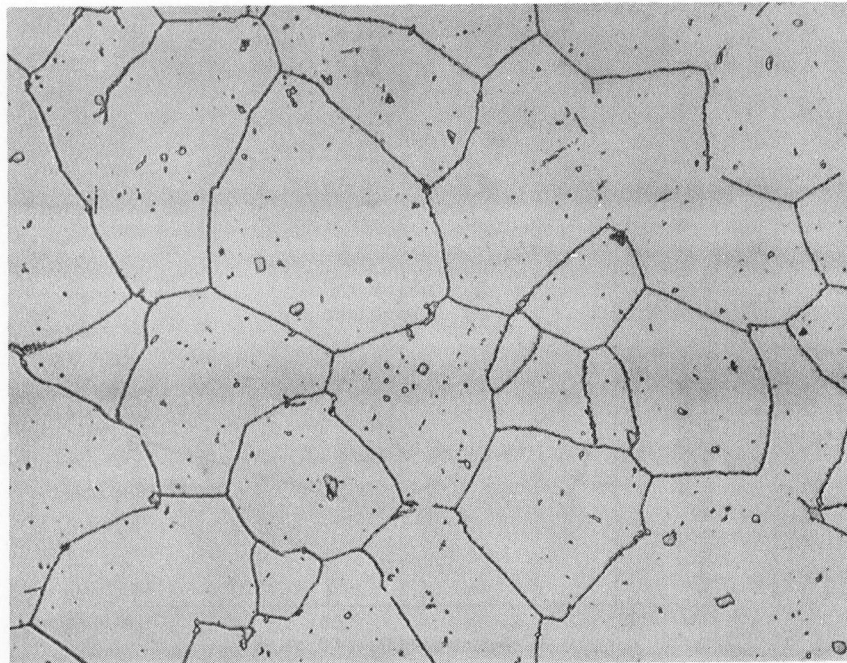


Figure 11. - Hydrogen permeability as a function of dopant level in pre-oxidized tubes with 1.0 vol. %  $\text{CO}_2$  at  $820^\circ \text{C}$  for 100 hr plus an additional 100 hr at  $820^\circ \text{C}$  with lower dopant levels.



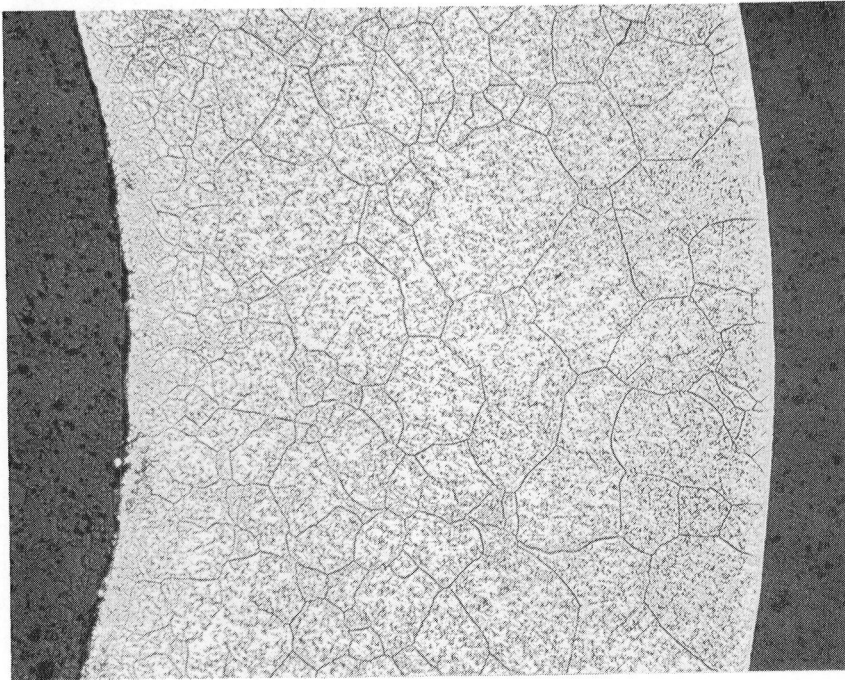
(a) 100X.



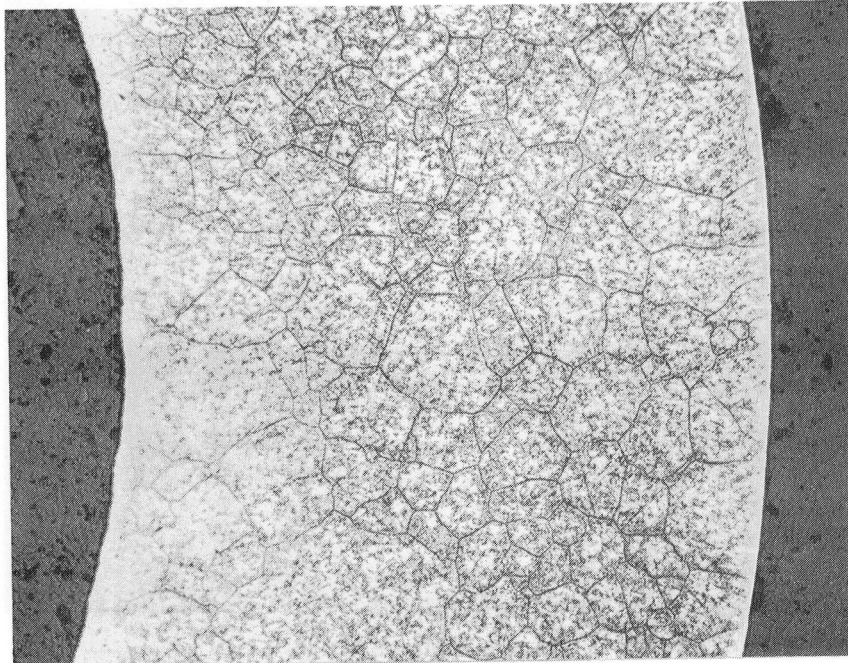
(b) 500X.

Figure 12. - Microstructure of As-heat treated CG-27 tubing.



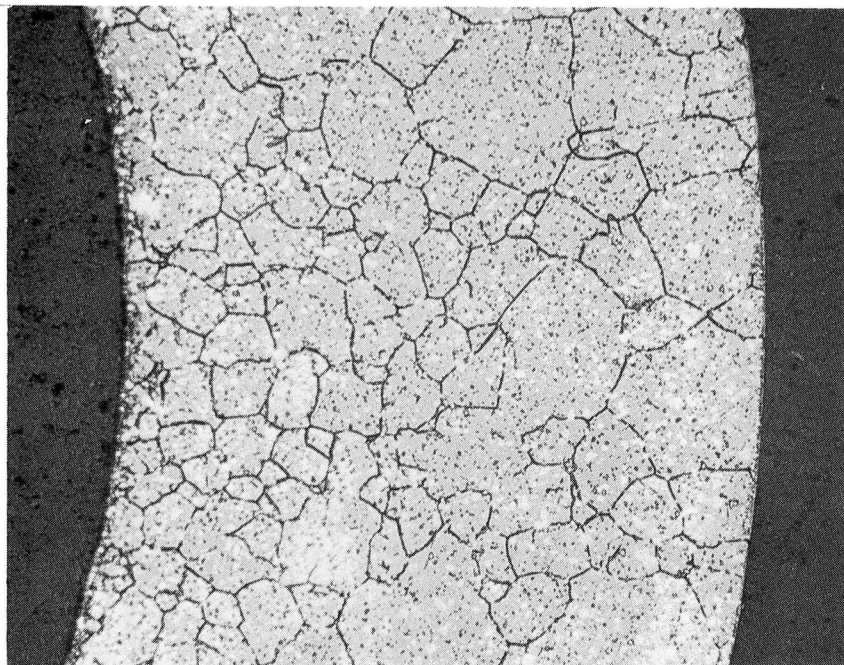


(a)  $H_2$  doped with 1.0 vol% CO.

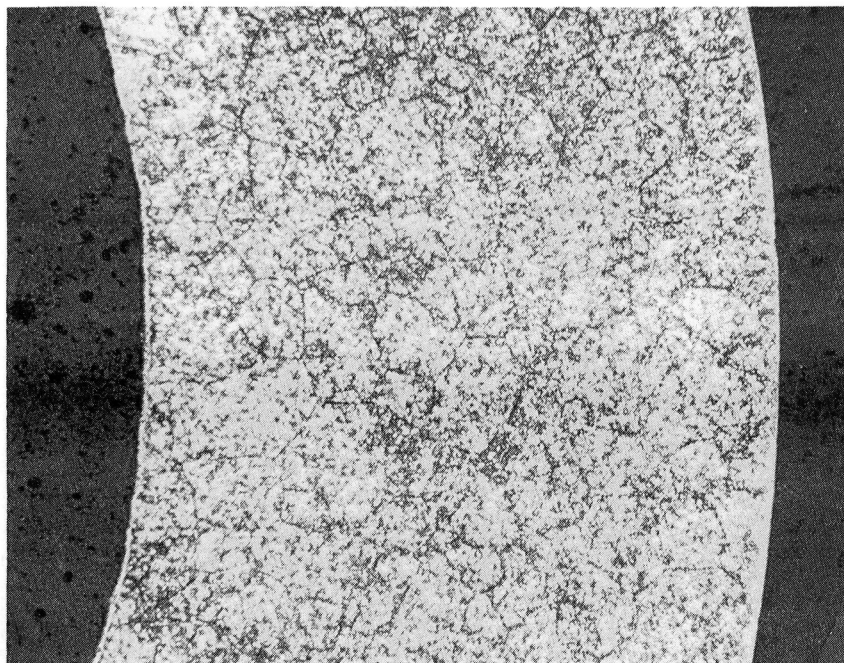


(b)  $H_2$  doped with 0.5 vol% CO.

Figure 13. - Microstructures of cross-sections of tubes exposed to hydrogen with various dopants for 100 hours at  $820^{\circ}C$ . Magnification 100X.

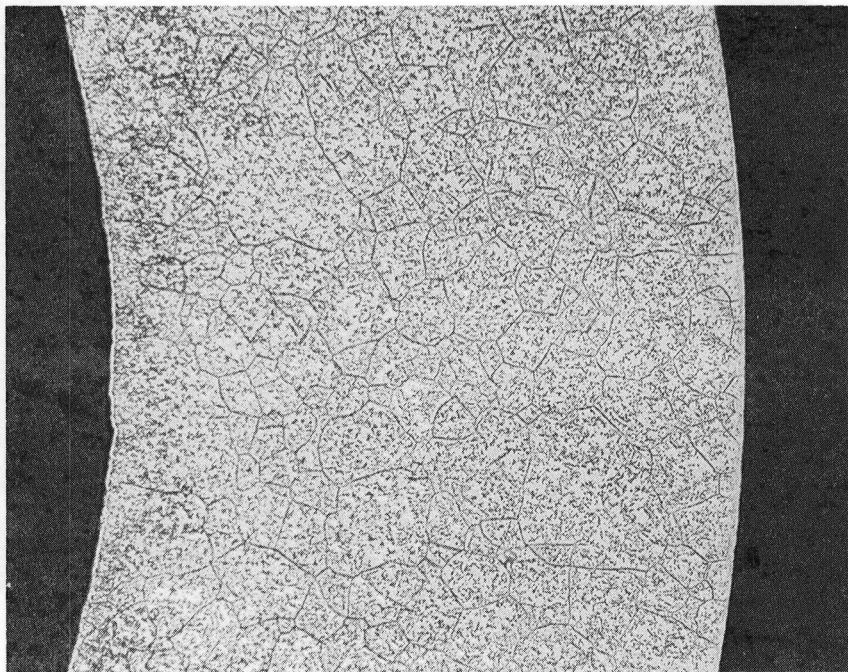


(c)  $\text{H}_2$  doped with 0.2 vol% CO.

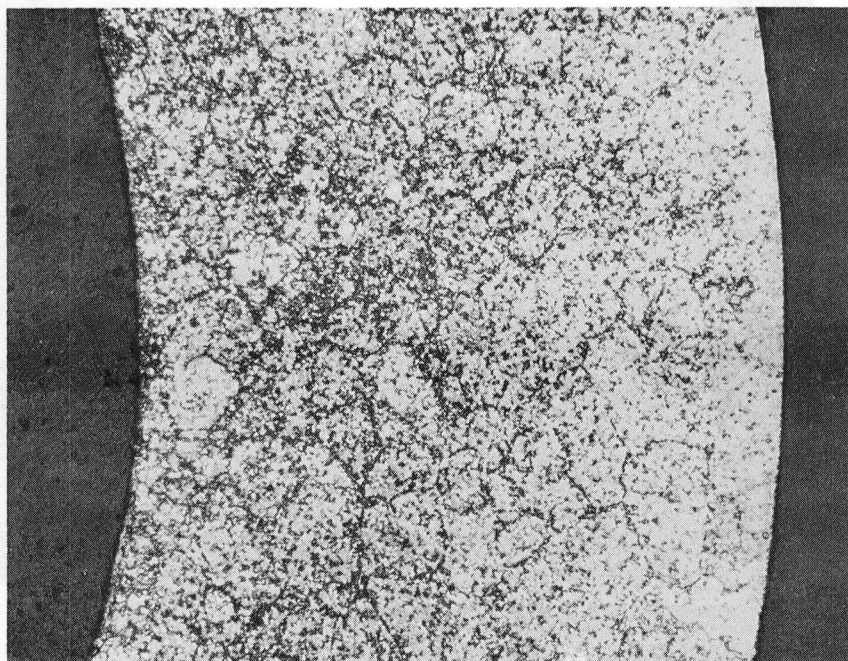


(d)  $\text{H}_2$  doped with 0.05 vol% CO.

Figure 13. - Continued.



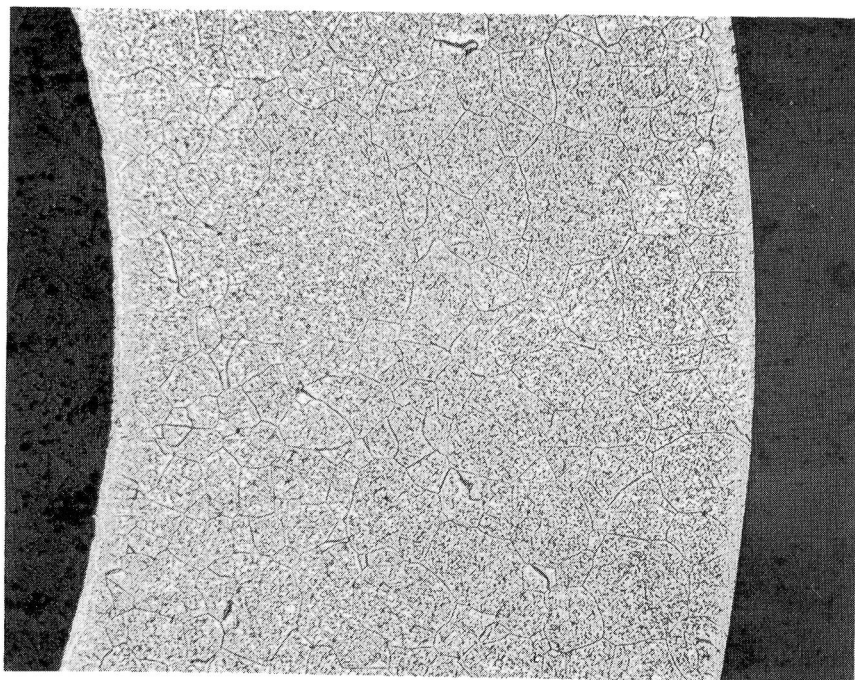
(e)  $\text{H}_2$  doped with 0.1 vol %  $\text{CO}_2$ .



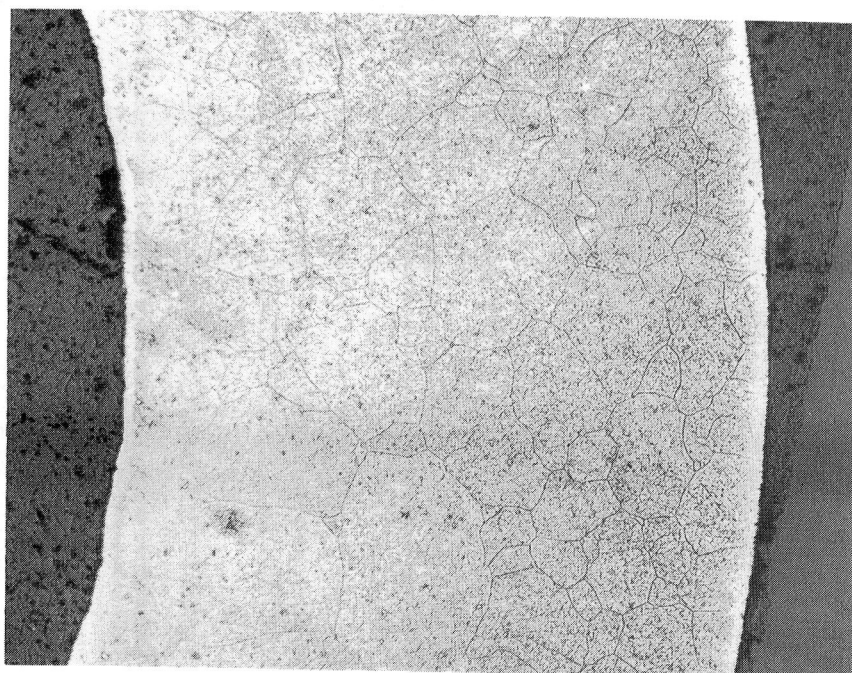
(f)  $\text{H}_2$  doped with 0.05 vol %  $\text{CO}_2$ .

Figure 13. - Concluded.



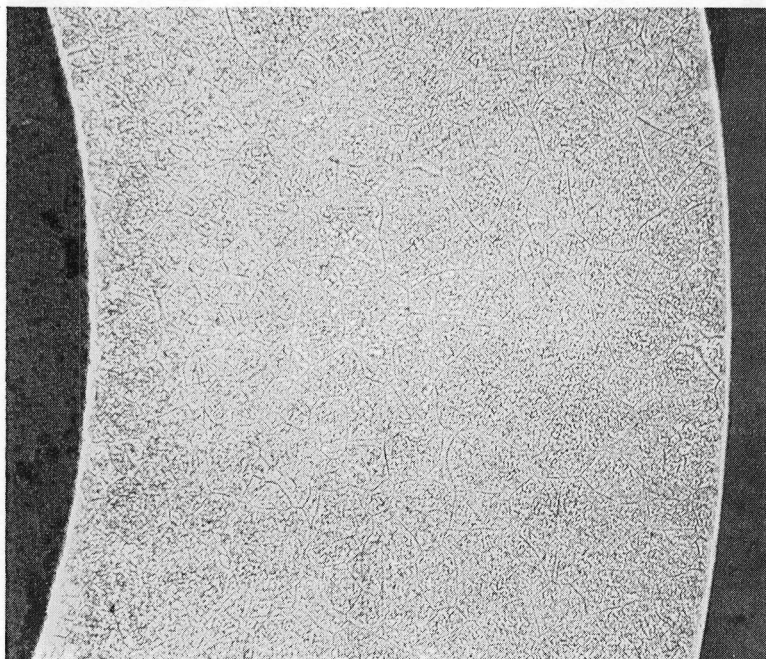


(a)  $H_2$  doped with 1.0 vol % CO.

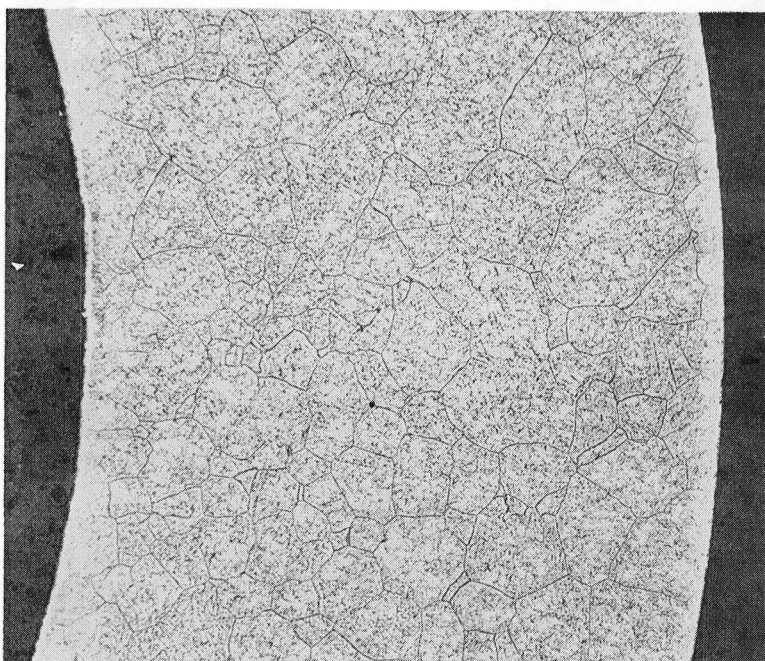


(b)  $H_2$  doped with 0.5 vol % CO.

Figure 14. - Microstructures of cross-sections of tubes pre-oxidized by exposure for 100 hours to hydrogen doped with 1.0 vol %  $CO_2$  and then exposed for an additional 100 hours to hydrogen doped with various dopants. Magnification 100X.

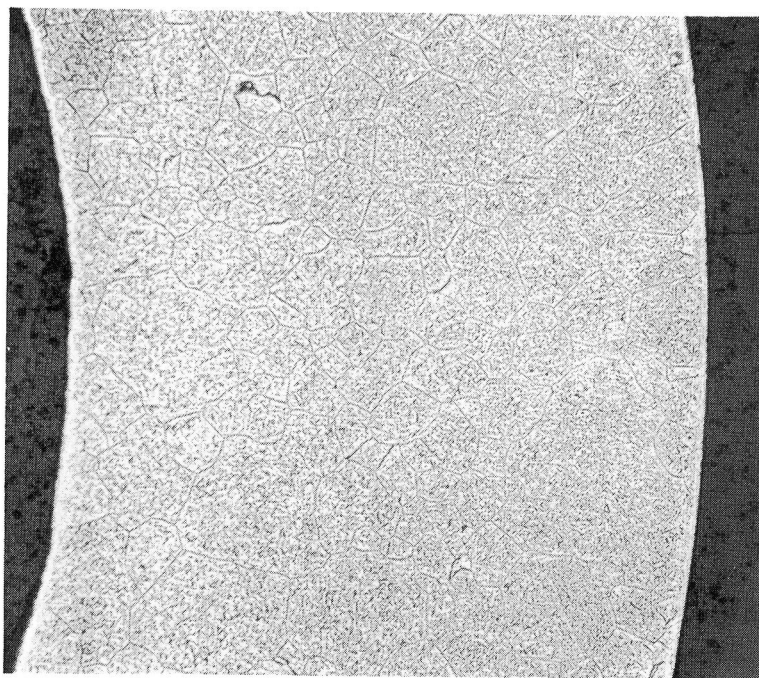


(c)  $H_2$  doped with 0.2 vol% CO.

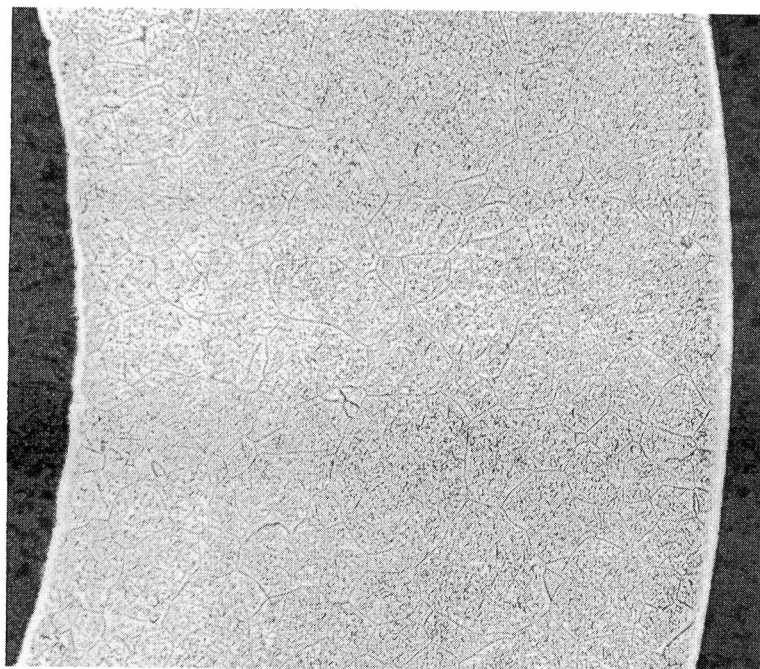


(d)  $H_2$  doped with 0.05 vol% CO.

Figure 14. - Continued.



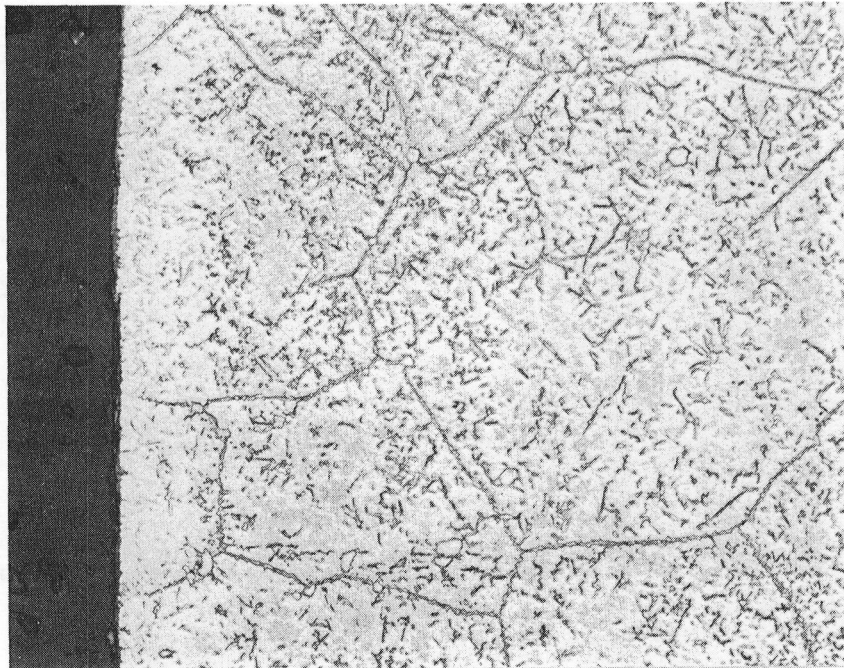
(e)  $\text{H}_2$  doped with 0.1 vol %  $\text{CO}_2$ .



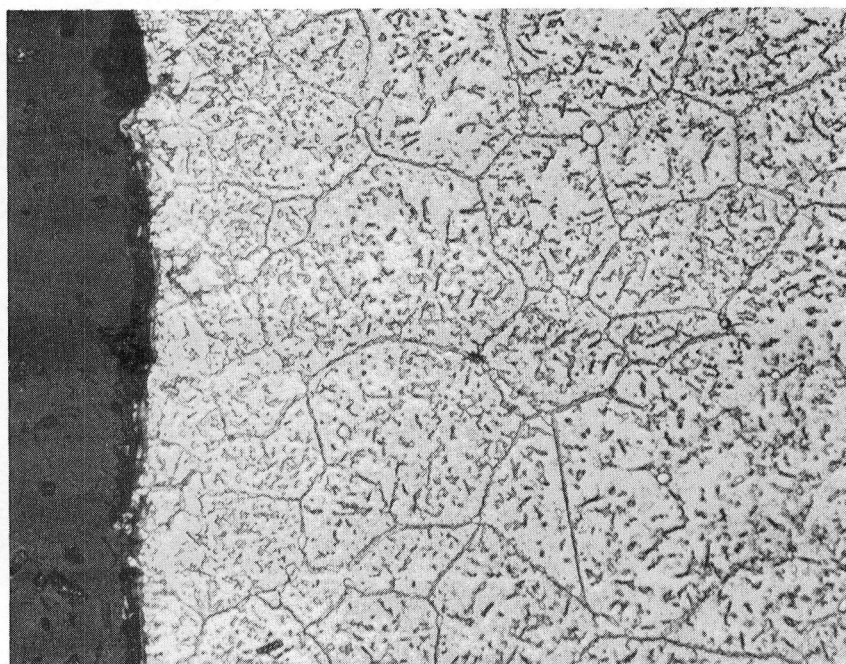
(f)  $\text{H}_2$  doped with 0.05 vol %  $\text{CO}_2$ .

Figure 14. - Concluded.



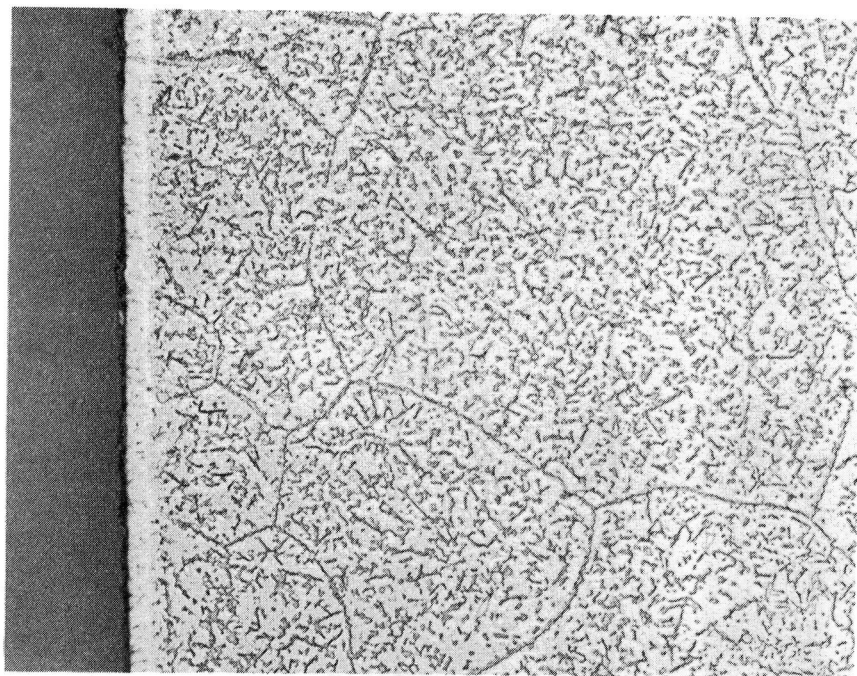


(a) Outer edge.

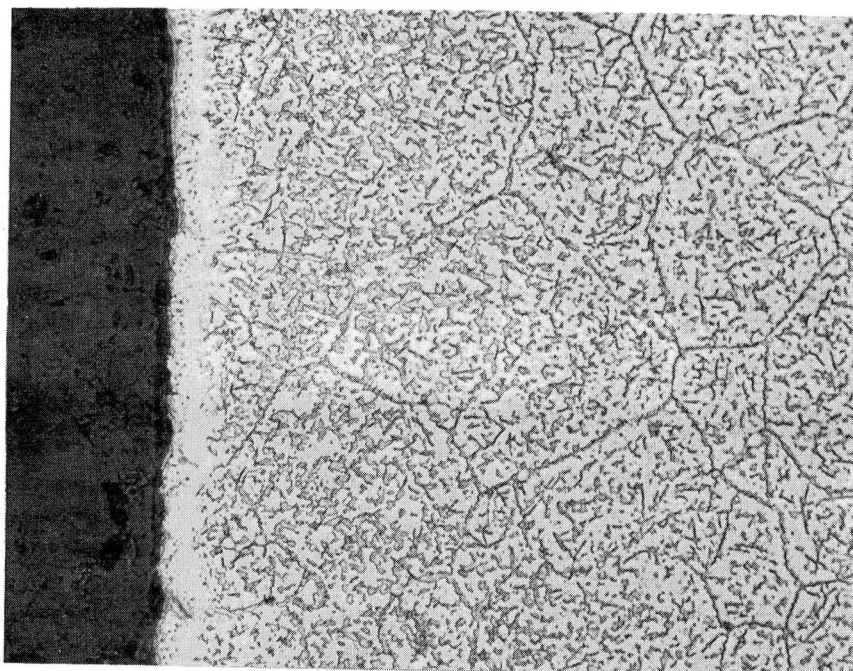


(b) Inner edge.

Figure 15. - Photomicrographs showing inner and outer edges of tube exposed for 100 hours to  $H_2$  doped with 1.0 Vol %  $CO_2$  and 100 hours to  $H_2$  doped with 1.0 Vol % CO (fig. 13a). Magnification 500 X.



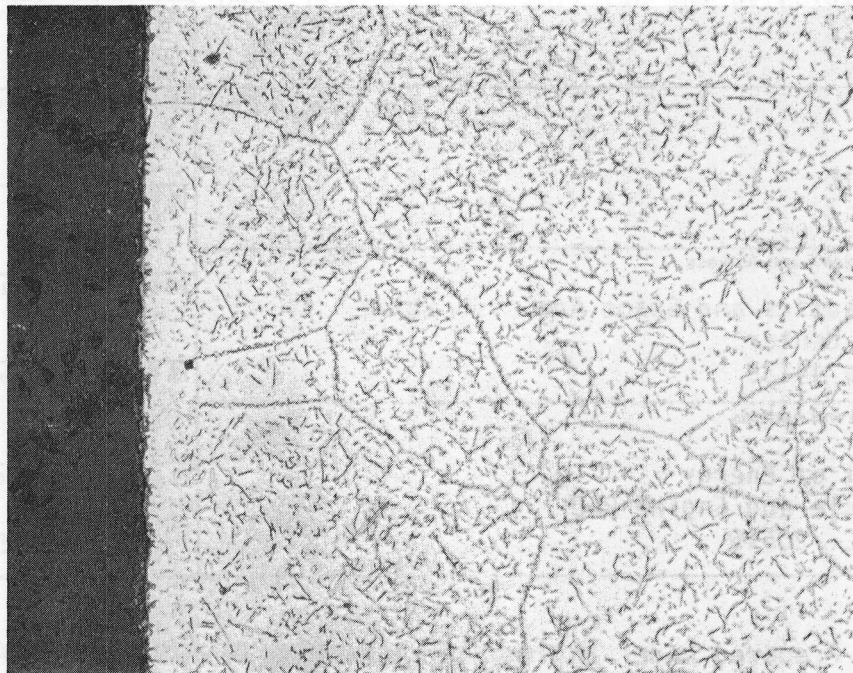
(a) Outer edge.



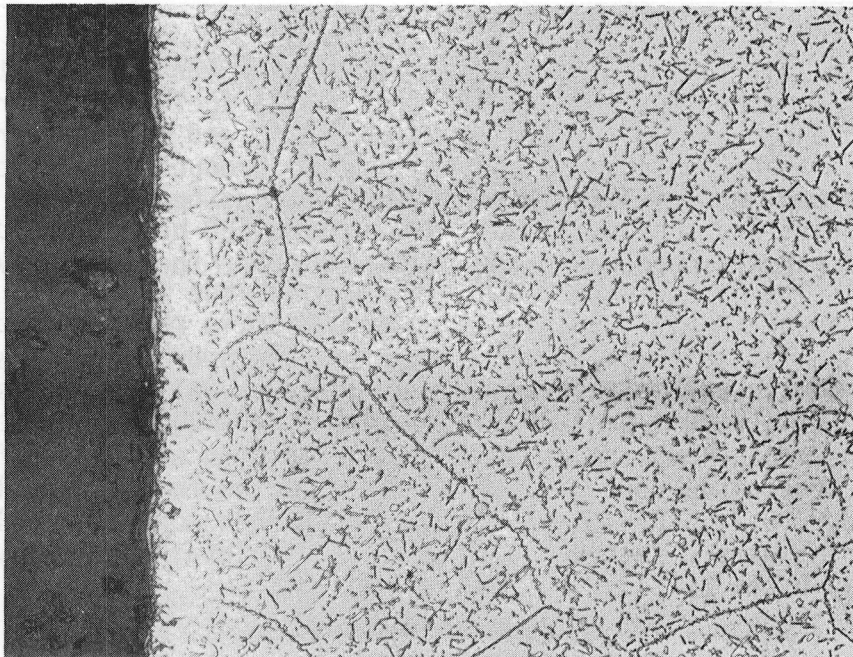
(b) Inner edge.

Figure 16. - Photomicrograph showing inner and outer edges of tube exposed for 100 hours to  $H_2$  doped with 1.0 Vol%  $CO_2$  and 100 hours to  $H_2$  doped with 0.2 Vol% CO (fig. 14c). Magnification 500X.





(a) Outer edge.



(b) Inner edge.

Figure 17. - Photomicrograph showing inner and outer edges of tube exposed for 100 hours to  $H_2$  doped with 1.0 Vol %  $CO_2$  and 100 hours to  $H_2$  doped with 0.1 Vol %  $CO_2$  (fig 14e). Magnification 500X.

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16. Abstract  Tubes of CG-27 alloy, filled with hydrogen doped with various amounts of carbon dioxide and carbon monoxide, were heated in a diesel-fuel-fired Stirling engine simulator materials test rig for 100 hours at 820° C and at a gas pressure of 15 MPa to determine the effectiveness of the dopants in reducing hydrogen permeation through the hot tube wall. This was done for clean as-heat treated tubes and also for tubes that had previously been exposed for 100 hours to hydrogen doped with 1.0 volume percent carbon dioxide to determine if the lower levels of dopant could maintain a low hydrogen permeation through the hot tube wall. Carbon dioxide, as a dopant in hydrogen, was most effective in reducing hydrogen permeation through clean tubes and in maintaining low hydrogen permeation after prior exposure to 1.0 volume percent carbon dioxide. Only the lowest level of carbon dioxide (0.05 volume percent) was not as effective in the clean or prior exposed tubes. Carbon monoxide as a dopant in hydrogen was less effective than carbon dioxide at a given concentration level. Of the four dopant levels studied; 1.0, 0.5, 0.2, and 0.05 volume percent carbon monoxide, only the 1.0 and 0.5 volume percent were effective in reducing and maintaining low hydrogen permeation through the CG-27.					
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